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Final Report

by

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OPTICAL PROPERTIES OF TRANSITION IONS IN CRYSTALS

UNDER BOMBARDMENT BY ENERGETIC PARTICLES,

X AND GAMMA RAYS AND LIGHT

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I. Scope of Work

The phenomena under study is the emission of light by crystals containing rare earth ions following excitation by various methods, including bombardment by energetic electrons, protons, etc., x and gamma rays and UV and visible light. Following absorption of energy by some process in the crystal, energy transfer processes carry a portion of the energy to low lying levels in the rare earth ions whereupon a portion is radiated as UV, visible and infrared light. The first (absorption) process, and the second (transfer) process will depend on the method of excitation. The last process (emission and competing radiationless processes) will generally be independent of the mode of excitation.

We have concentrated on elucidating the role of the radiationless processes and their effect on the lifetimes of the radiating states because this is probably the simplest part of the whole chain to understand.

II. Time Resolved Spectrometry

Because the method of excitation is of little importance to the study of the terminal processes, we used the most convenient source, a flash lamp. We wished to measure fluorescence intensity versus time after excitation in order both to observe the build up of population in the low levels by process two (transfer) and the decay of population by process three (radiation and radiationless processes). Figure 1 is a

block diagram of the equipment used. The timing is controlled by a Tektronix 181 Time Mark Generator, which consists of a crystal controlled oscillator at 10 Mc/sec, and decade scalars. The output pulse every 10 m sec triggers the flash lamp and starts a timing circuit consisting of Tektronix 162 and 161 pulsers. The former generates a ramp which is fed to the 161 pulser. At a selected point on the ramp, the 161 is triggered and drives a keyer for the photomultiplier tube. The delay between the flash and the photomultiplier "on" pulse can be varied from 1 μ sec to 10 m sec. The photomultiplier "on" pulse was adjusted in the range 10 μ sec to 5 m sec. The photo current was averaged for 1 to 10 sec. and displayed on a chart recorder.

III. Materials Studied

A wide variety of crystals containing rare earths as doping were studied in order to find the optimum system for study of the radiationless decay processes. These included

Sm ²⁺ :KCl	Ce ³⁺ :LaF ₃
Sm ²⁺ :LaCl ₃	Pr ³⁺ :LaF ₃
Sm ²⁺ :LaF ₃	Nd ³⁺ :LaF ₃
Pr ³⁺ :LaCl ₃	Eu ³⁺ :LaF ₃
Nd ³⁺ :LaCl ₃	Dy ³⁺ :LaF ₃
Sm ³⁺ :LaCl ₃	Ho ³⁺ :LaF ₃
Er ³⁺ :CaWO ₄	Er ³⁺ :LaF ₃
Pr ³⁺ :CaWO ₄	Tm ³⁺ :LaF ₃
Nd ³⁺ :CaWO ₄	
Pr ³⁺ :CaF ₂	
Nd ³⁺ :CaF ₂	
Sm ³⁺ + Sm ²⁺ :CaF ₂	
Er ²⁺ :CaF ₂	
Tb ³⁺ :CaF ₂	
Dy ³⁺ :CaF ₂	
Ho ³⁺ :CaF ₂	
Er ³⁺ :CaF ₂	
Tm ³⁺ :CaF ₂	
U ³⁺ :CaF ₂	

In addition, LaCl_3 crystals with two rare earth dopings (one always Sm^{2+}) were studied for possible energy transfer between the Sm^{2+} and the other rare earth ions. Each of the 13 rare earths was tried as a second dopant.

IV. Results

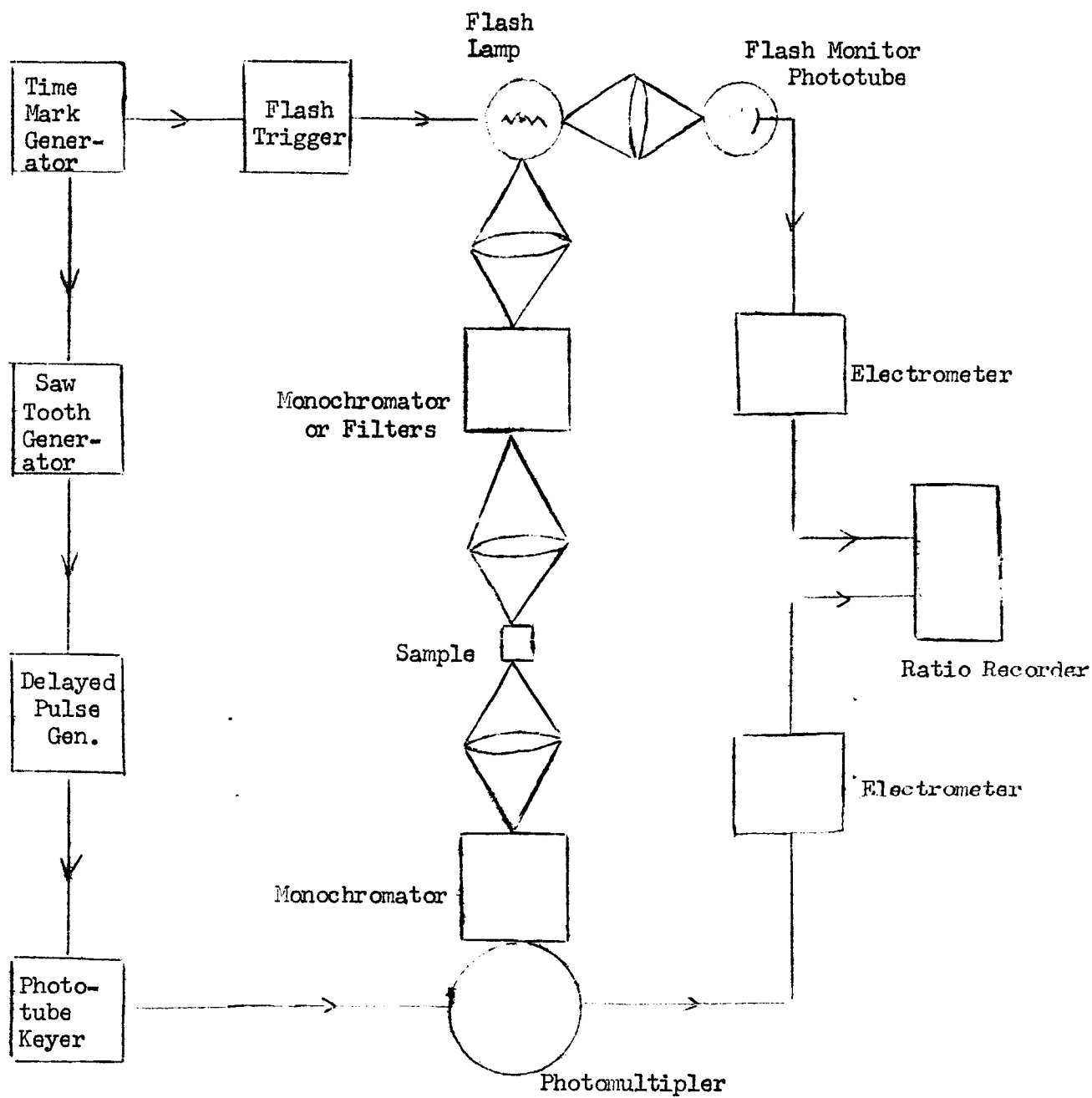
Results obtained that have been published so far are: (1) A paper containing preliminary results on $\text{Pr}^{3+}:\text{LaCl}_3$, $\text{Nd}^{3+}:\text{LaCl}_3$ and $\text{Sm}^{2+}:\text{LaCl}_3$. These include rise lifetimes for Sm^{2+} and fall lifetimes for all, at 77°K and 4.2°K. Also, the excitation spectrum of Sm^{2+} was determined. Reprints of this paper are appended. Further work on $\text{Sm}^{2+}:\text{LaCl}_3$ was reported (2) at the Southeastern Section Meeting of the American Physical Society. This included a discussion of the spectra and lifetimes of the two Sm^{2+} sites existing in the LaCl_3 crystal. An abstract of this paper is appended.

In his Dissertation (3), Dr. Partlow gave results of a careful temperature dependence measurement on the $\text{Sm}^{2+}:\text{LaCl}_3$ lifetimes. He found a striking dependence which indicates a multiphonon process; on the order of 20 phonons, with energy 50 cm^{-1} each, being generated by stimulated emission to act as the radiationless process which depopulates the excited level of Sm^{2+} . This assumes importance in the temperature region 50 - 70°K. A paper setting forth these results is being prepared and reprints will be sent when they are ready.

V. Publications by this Report

- (1) W. D. Partlow and E. H. Carlson, "Fluorescence Decay of Pr^{3+} , Nd^{3+} , and Sm^{2+} in LaCl_3 ," J. Chem. Phys. 41, 3645 (1964).
- (2) E. H. Carlson and W. D. Partlow, "Fluorescence Rise and Decay Lifetimes of Sm^{2+} in LaCl_3 ," Bull. Am. Phys. Soc., Ser. II, 10, 262 (1965).
- (3) W. D. Partlow, "Fluorescence Decay of the Sm^{2+} Ion in Lanthanum Chloride," Ph.D. Dissertation, University of Alabama (1965).
- (4) A paper on the temperature dependence of $\text{Sm}^{2+}:\text{LaCl}_3$ is being prepared, and reprints will be sent when available.

TIME RESOLVED SPECTROMETER



Fluorescence Decay of Pr^{3+} , Nd^{3+} , and Sm^{2+} in LaCl_3 [†]

W. D. PARTLOW AND E. H. CARLSON

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(Received 11 September 1964)

DECAY curves for various levels of Pr^{3+} , Nd^{3+} , and Sm^{2+} in LaCl_3 single crystals were obtained by measuring¹ the intensity of fluorescence lines as a function of the time after illuminating the crystal with a repetitively flashed EG&G FX-6A flash lamp. The intensity was measured by applying a pulse² to an EMI 9558B photomultiplier tube. Measurements were made both at 77° and 4.2°K. Selective excitation wavelengths were obtained both by using filters and monochromators. The results are displayed in Table I.

The findings for Sm^{2+} are of special interest. Fluorescence is observed within the $4f^8$ configuration from two 4D levels (*A* and *B*) about 1300 cm^{-1} apart to the 7F ground multiplet. The excitation of *A* and *B* is probably due to nonradiative transitions from levels of the $4f^65d$ configuration, which may be populated by allowed transitions from the ground state.³

When observed with steady-state apparatus, the fluorescence from *A* is more intense than that from *B* at 77°K. The opposite is true at 4.2°K. We note also that the lifetime of the *B* level is the same at 77° and 4.2°K. The relative intensity increase from *A* at 77°K indicates a temperature-dependent excitation process and the intensity-versus-time curve for *A* at 77°K shows an initial rise followed by decay. The rise time of *A* at 77°K is $50\% \pm 5\%$ μsec while the decay time of *B* is $2000\text{ }\mu\text{sec}$. Thus the $B \rightarrow A$ nonradiative process found in isoelectronic Eu^{2+} chelate⁴ does not obtain here.

The excitation spectrum (fluorescence intensity versus exciting wavelength) was obtained for the fluorescing levels of Sm^{2+} and is shown in Fig. 1. No difference could be detected between the excitation spectra for *A* and *B* nor between 77° and 4.2°K. We

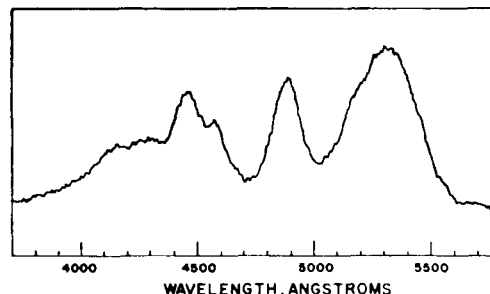


FIG. 1. Excitation spectrum for the $B \rightarrow W$ transition of Sm^{2+} at 4.2°K. Excitation is by a tungsten lamp through a monochromator with a band pass of 60 Å.

conclude either that the *A* level is populated at 77°K from a higher level (not *B*) of the $4f^8$ configuration, or that some Sm^{2+} ions in special lattice sites have a rapid conversion $B \rightarrow A$ at 77°K (giving a rise time of 50 μsec to the *A* fluorescence and quenching the *B* fluorescence) while others do not (giving rise to a weaker *B* fluorescence with a "normal" lifetime of $2000\text{ }\mu\text{sec}$).

No structure was found in the peaks of the excitation spectrum using a resolution of 1.6 Å, and it is concluded that the broad peaks represent absorption bands in the $4f^65d$ configuration.

[†] This work was supported by the National Aeronautics and Space Administration under contracts NAS8-5029 and NAS8-11200.

¹ G. E. Peterson and P. M. Bridenbaugh, J. Opt. Soc. Am. **52**, 1079 (1962).

² We wish to thank D. E. Kerr for several helpful discussions on instrumentation and for the loan of equipment in the early stages of this work.

³ G. H. Dieke and R. Sarup, J. Chem. Phys. **36**, 371 (1962).

⁴ M. L. Bhaumik, J. Chem. Phys. **41**, 574 (1964).

TABLE I. Fluorescence decay lifetimes of Pr^{3+} , Nd^{3+} , and Sm^{2+} in LaCl_3 .

Material ^a	Ion	Level	Decay time (microseconds)	
			4.2°K	77°K
5 % Pr	Pr^{3+}	$^4P_0(0)$	25 ^c	
0.1 % Nd	Nd^{3+}	D^0	$34 \pm 10\%$	
0.1 % Nd	Nd^{3+}	E^0	$76 \pm 5\%$	
0.1 % Nd	Nd^{3+}	F^0	$85 \pm 5\%$	
0.01 % Sm	Sm^{2+}	A^4	$10\ 000^c$	$3500 \pm 5\%$
0.01 % Sm	Sm^{2+}	B^4	$2000 \pm 5\%$	$2100 \pm 5\%$

^a Given is the nominal concentration of the rare-earth chloride added to LaCl_3 before growing the crystals.

^b G. H. Dieke and R. Sarup, J. Chem. Phys. **29**, 761 (1958).

^c E. H. Carlson and G. H. Dieke, J. Chem. Phys. **34**, 1082 (1961).

^d Reference 3 of the paper.

^e Order-of-magnitude estimate.

Southeastern Section of the American Physical Society, Chattanooga,
November 5-7, 1964

Fluorescence Rise and Decay Lifetimes of Sm^{2+} in LaCl_3 , W. D. PARTLOW
(Introduced by W. G. Moulton) AND E. H. CARLSON, University of Alabama

Time resolved spectroscopy by means of sample illumination by repetitive flash and time-delayed pulsing of a photomultiplier detector was utilized. Various wavelength regions in the excitation were obtained by filters and a monochromator. At 4.2°K, no initial rise in fluorescence intensity as a function of time after the flash could be seen. Decay lifetimes were 10 msec and 2 msec for the A and B levels¹ respectively. At 77°K, the fluorescence from A showed an initial rise with a lifetime of 50 μsec and a decay of 3.5 msec. The B showed only a decay time of 2.1 msec. Possible explanations for this behavior will be discussed.

¹G. H. Dieke and R. Sarup, J. Chem. Phys. 36, 371 (1962).